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Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties

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Abstract

Torrefaction is a treatment which serves to improve the properties of biomass in relation to thermochemical processing techniques for energy generation; for example, combustion, co-combustion with coal or gasification. The topic has gathered interest in the past two decades but further understanding is required for optimisation of the process thus enhancing economic efficiency, which is crucial to the success of the treatment commercially and within industry. In particular there is a noticeable gap in current literature regarding the combustion properties of torrefied biomass. This study examines torrefaction in nitrogen of two energy crops, reed canary grass and short rotation willow coppice (SRC), and a residue, wheat straw. Product evolution and mass and energy losses during torrefaction are measured using a range of laboratory scale methods. Experiments at different torrefaction conditions were undertaken to examine optimization of the process for the three fuels. Progress of torrefaction was also followed by chemical analysis (C, H, N, O, ash), and it was seen that the characters of the biomass fuels begin to resemble those of low rank coals in terms of the van Krevelen coal rank parameter. In addition, the results indicate that the volatile component of biomass is both reduced and altered producing a more thermally stable product, but also one that produces greater heats of reaction during combustion. The difference between the mass and energy yield was shown to improve for the higher torrefaction temperatures investigated. The combustion behaviour of raw and torrefied fuels was studied further by differential thermal analysis (DTA) and also, for willow, by suspending individual particles in a methane–air flame and following the progress of combustion by high-speed video. It is shown that both volatile and char combustion of the torrefied sample become more exothermic compared to the raw fuels, and that depending on the severity of the torrefaction conditions, the torrefied fuel can contain up to 96% of the original energy content on a mass basis. Upon exposure to a methane-air flame, torrefied willow ignites more quickly, presumably because its low moisture content means that it heats faster. Torrefied particles also begin char combustion quicker than the raw SRC particles, although char combustion is slower for the torrefied fuel.

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1. Introduction

Biomass is a unique fuel and has the potential to play a significant role in the future energy mix in the UK. Unlike other renewables, biomass can provide continuous electricity generation, and is the only widespread source of renewable heat. Increased use of biomass as a source of energy (electricity and heat) will contribute to the reduction of CO_2 emissions, increase energy security, and support sustainable development and regeneration of rural areas, both through increased agricultural and forestry activity and the provision of small scale localised energy and heat generation schemes [1].

However, renewables still only account for a minute proportion of energy generation in the UK. In 2005, 4.2% of electricity was generated by renewable sources, 53% of which was from biomass and wastes (including MSW (municipal solid waste), animal waste, forestry

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residues, industrial and domestic wood, co-fired generation and short rotation coppice) [2]. However, in 2004 renewable heat generated from biomass and biofuels accounted for just 1% of the total heat market [1]. Evidently there are a number of obstacles to overcome in order to expand the biomass sector and the use of biofuels. Whilst some of these include bureaucracy, economics and fragmented approaches from regional and national authorities, there are also limitations associated with biomass fuel properties.

Direct comparisons of biomass with coal, still the dominant solid fuel in electricity and heat generation, often reveal inferior properties of biomass. In particular, it has lower energy densities, is a bulkier fuel (with poorer handling and transportation characteristics), more tenacious (its fibrous nature means it is difficult to reduce to small homogeneous particles) and – in most cases – a higher moisture content, resulting in storage complications such as degradation and self heating. These properties can have negative impacts during energy conversion such as lower combustion efficiencies and gasifier design limitations.

Torrefaction is a thermal treatment that occurs in an inert atmosphere. It removes moisture and low weight organic volatile components and depolymerises the long polysaccharide chains, producing a hydrophobic solid product with an increased energy density (on a mass basis) and greatly increased grindability. As a result, significantly lower energy is require to process the torrefied fuel and it no longer requires separate handling facilities when co-fired with coal in existing power stations. (In 2005, 15% of all renewable electricity generation in the UK was from biomass co-fired with coal [2].) It has also been suggested that the modified fuel can be compacted into high grade pellets with substantially superior properties when compared with standard wood pellets. The process can be incorporated into a combined drying, torrefaction and pelletisation process, with both economic and energy efficiency benefits [3]. Finally, it has been suggested that torrefied biomass is a suitable feedstock for entrained flow gasification, systems previously not considered feasible for raw biomass solid fuels. This is because torrefied biomass forms more spherical shaped particles during grinding or milling [4]. However, the process requires a separate plant, an input of process energy and the production of gaseous and volatile streams, entailing capital costs, operating costs and emission control. The balance between these associated costs and energy consumption and the cost and energy benefits from a more grindable, higher calorific value fuel are therefore critical for the future of torrefaction and require thorough analysis and reliable, extensive data. A evaluation of the torrefaction of wood chips published in 2001 concluded that the environmental and heating value benefits gained by torrefaction are not significantly greater than the extra energy consumption and capital investment [5], although it did indicate potential for the torrefaction concept in fuel densification. However, a number of other publications are optimistic about the benefits torrefaction has to offer. Furthermore, there are concepts such as retrofitting existing power stations in order to ultilise waste heat to serve a torrefaction process plant which must be considered.

Torrefaction has only received significant interest in the last two decades, and has yet to become a commercial process. The majority of research to-date has focused on the compositional changes that occur in biomass, determined by proximate and ultimate analysis, along with mass and energy yields [6–8]. Some studies have also investigated the composition of volatile matter released during the process [9,10]. This previous work has focused primarily on woody biomass, including the comparisons of softwoods and hardwoods. Energy crops have received little attention, and there is still a need for comprehensive understanding of the optimum torrefaction conditions, as well as investigations of the combustion behaviour of these fuels, including the emissions and smoke compositions from torrefied fuels. Work presented in this paper reports on fundamental investigations into torrefaction of an energy grass, and makes comparisons with a woody biomass (willow) and an agricultural bi-product (wheat straw). In the second half of the paper combustion properties of all three fuels are investigated. The results from this paper will contribute to further work involving economic analysis of this pretreatment, which is beyond the scope of this paper.

2. Experimental procedure

2.1. Torrefaction process

2.1.1. Samples

Two energy crops and an agricultural residue, namely willow (short rotation coppice, SRC), reed canary grass and wheat straw respectively, have been torrefied with subsequent analysis of the solid residues. These types of lignocellulose biomass material cover two of the three solid biofuel categories currently being considered as suitable for thermochemical conversion processes in the UK. Standard DD CEN/TS 14961:2005 [11] categorises willow (short rotation coppice) as woody biomass (forest and plantation wood), whilst reed canary grass (grasses) and wheat straw (cereal crops) are classed as herbaceous biomass.

The reed canary grass and wheat straw were grown at the Woburn Experimental Farm in Bedfordshire, UK, part of Rothamsted Research. The SRC willow was grown by Rural Generation in Northern Ireland.

2.1.2. Evolved gas analysis by TGA-FTIR

A Nicolet Magma-IR AEM connected to a Stanton Redcroft Simultaneous Analyser STA-780 Series was used to perform torrefaction experiments at laboratory scale whilst simultaneously analysing the volatile pyrolysis products for corresponding TGA data. Samples weighing between 25 and 35 mg were placed in a nickel crucible. The temperature was ramped to 378 K at 10 K min^{-1} and held for 5 min in order to remove moisture. The second stage of the regime used the same ramp rate to reach the desired torrefaction temperature in the range 503–563 K. The inert atmosphere was maintained using nitrogen at STP at a flow rate of 50 ml min^{-1}. It is widely accepted in the literature that the onset of primary pyrolysis occurs at 473 K [e.g. 12,13]. The time period between this temperature being reached and the point of cooling has previously been defined as the 'torrefaction time' [4]. Each run was carried out so that this time interval was 30 min.

2.1.3. Ultimate analysis

The C, H, N, O, S contents are measured using a CE Instruments Flash EA 1112 Series elemental analyzer. All measurements were repeated in triplicate and a mean value corrected for moisture content is reported. The ash content of the raw samples was measured in a Carbolite OAF 10/1 furnace, adhering to standard DD CEN/TS 14775:2004 [14]. It was assumed that no ash will be lost during the pyrolysis stage thus an ash content value has been calculate for each solid residue from overall mass yields.

2.1.4. Cell wall composition

Lignin, cellulose and hemicellulose were determined at the Institute of Grassland and Environmental Research, Aberystwyth, UK, via Klason, Acid Digestible Fibre (ADF) [15], and Neutral Digestible Fibre (NDF) [16] wet chemistry methods. Briefly these procedures entail the following: ADF was determined by detergent incubation under acid (pH 2) conditions. The sample was boiled and filtered, hemicellulose and cell solubles dissolve and are filtered away. The residue left is ADF and consists mainly of cellulose and lignin. Acid detergent lignin (ADL) was measured by further treating ADF with strong acid, which dissolves cellulose. The cellulose content was derived by subtracting ADF values from ADL values.

2.2. Fuel analysis

2.2.1. Calorific value determination

Friedl et al. [17] provide a method using two equations for the calculation of CV based on the carbon, hydrogen and nitrogen content: an ordinary least squares regression (OLS) (Eq. (1)) and a partial least squares regression (PLS) method (Eq. (2)). These were calibrated using 122 different biomass samples and give the higher heating value (HHV) on a dry basis.

$$\mathrm{HHV(OLS)} = 1.87\mathrm{C}^2 - 144\mathrm{C} - 2802\mathrm{H} + 63.8\mathrm{CH} + 129\mathrm{N} + 20147 \quad (1)$$

$$\mathrm{HHV(PLS)} = 5.22\mathrm{C}^2 - 319\mathrm{C} - 1647\mathrm{H} + 38.6\mathrm{CH} + 133\mathrm{N} + 21028 \quad (2)$$

where C = carbon, H = hydrogen, and N = nitrogen content expressed on a dry mass percentage basis. Calorific values are reported are calculated using an average of the results from both two methods and further corrected for ash content to give a calorific value on a dry ash free basis.

2.2.2. Thermogravimetric analysis (TGA)

Pyrolysis tests were performed using a TGA analyser (Stanton Redcroft Simultaneous Analyser STA-780 Series), by heating a typical sample mass of 3 mg in a purge of nitrogen (50 ml min^{-1}), at a rate of 20 K min^{-1}. The final temperature was 1173 K, with a holding time of 15 min. Burning profiles of the four samples were performed using a DTA analyser (Stanton Redcroft Simultaneous Analyser STA-780 Series). A typical sample mass of 3 mg was heated at 20 K min^{-1} in a purge of air (50 ml min^{-1}) to a final temperature of 1173 K. Both thermogravimetric and differential temperature measurements were recorded simultaneously during combustion analysis.

2.2.3. Combustion studies

A Meker-burner was used to conduct combustion studies of stationary willow and torrefied willow particles (prepared using the TGA procedure described above). The Meker-burner flame consists of a number of short blue inner cones and a large single outer flame reaction zone which approximates to a 1D flame. Natural gas was used and the stoichiometry controlled so that the part of the flame in which the particles were placed reached a temperature of ~1500 K. The oxygen content at this location was 1.75 mol%. The particles (2–4 mm in length) were held in place on a steel needle adjacent to an R-type thermocouple in a ceramic housing. A water-cooled probe surrounded both the particle and the thermocouple before entry into the flame. The probe is placed into the flame ensuring that the particle and thermocouple are located centrally above the burner. The water-cooled sleeve is then retracted so that the particle and thermocouple are exposed to the flame. Upon completion of particle combustion, the water-cooled sleeve is slid back over the needle and thermocouple and the unit is removed from the flame. A Photo-Sonics Phantom V7 high-speed video system was used to record the images of the combusting particles at a speed of 1000 frames per second (fps). The captured footage was used to observed the combustion behaviour and determine the duration of different combustion stages. Further experimental details can be found in [14].

3. Results and discussion

3.1. Torrefaction process

3.1.1. TGA-FTIR torrefaction

Fig. 1 illustrates the influence of temperature and residence time on the final mass yield of the solid residue. At 503 K there was only slight reduction in mass and less than the amount of moisture lost during drying. However, increasing temperature has a marked affect on the thermal decomposition of the biomass; for temperatures of 563 K mass losses of 27–38% were observed for the three samples on a dry basis. The greatest rate of mass loss occurred during the temperature ramping stage but the isothermal period accounts for the greatest overall mass loss, with the

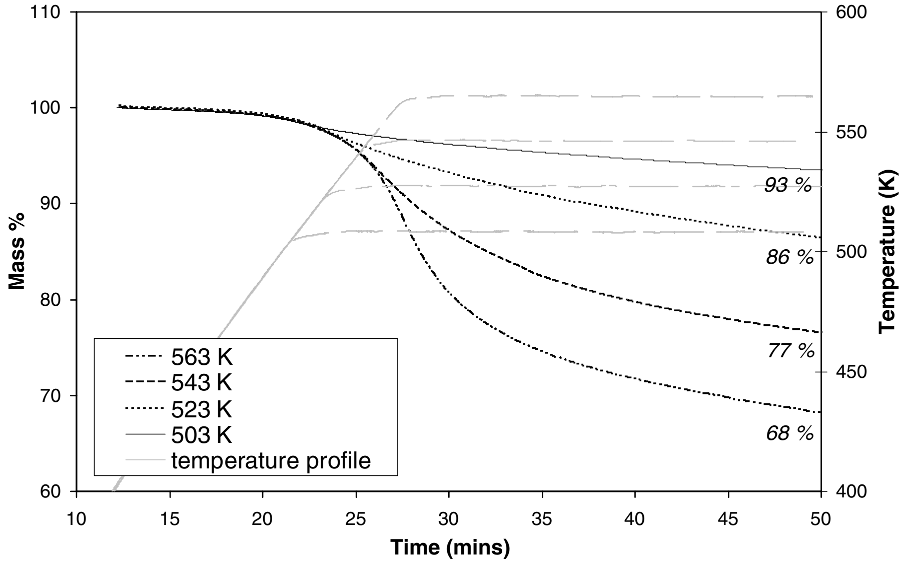

Fig. 1. Mass loss during the torrefaction of reed canary grass at different final temperatures.

exception of reed canary grass treated at 563 K, and suggests that heating rate is a critical parameter of the process.

Fig. 2 gives a comparison of the mass loss profiles at 563 K of different samples. The greatest mass losses at all the temperatures investigated occurred in wheat straw although they were similar to that observed for reed canary grass, whilst the lowest change in mass was observed for willow. The difference in the cell wall composition (Table 1) provides an explanation for these differences. Hemicellulose is the most reactive of the three lignocellulose components found in biomass and during torrefaction it will undergo the most significant decomposition reactions. Thus the composition of biomass fuels has a significant impact on the amount of both solid residue remaining and the volatile and gaseous products evolved during torrefaction. Wheat straw and reed canary grass have similar compositions whilst willow has a noticeably lower amount of hemicellulose but higher levels of cellulose and lignin. Metal content and composition is also expected to play a role [18,19], and this will be the subject of further study.

Studies conducted using xylan (the prominent hemicellulose found in herbaceous biomass) have concluded that decomposition of hemicellulose starts at temperatures above 473 K and full devolatisation will occur by 623 K, with the major products being H_2O, CO_2, CO, and char, as well as traces or low molecular weight organics [20]. Pure cellulose has a comparatively slower decomposition process at temperatures in excess of 523 K, and the rate of thermal decomposition only becomes more rapid above 573 K. In the 523–573 K range up to 20–30% of the

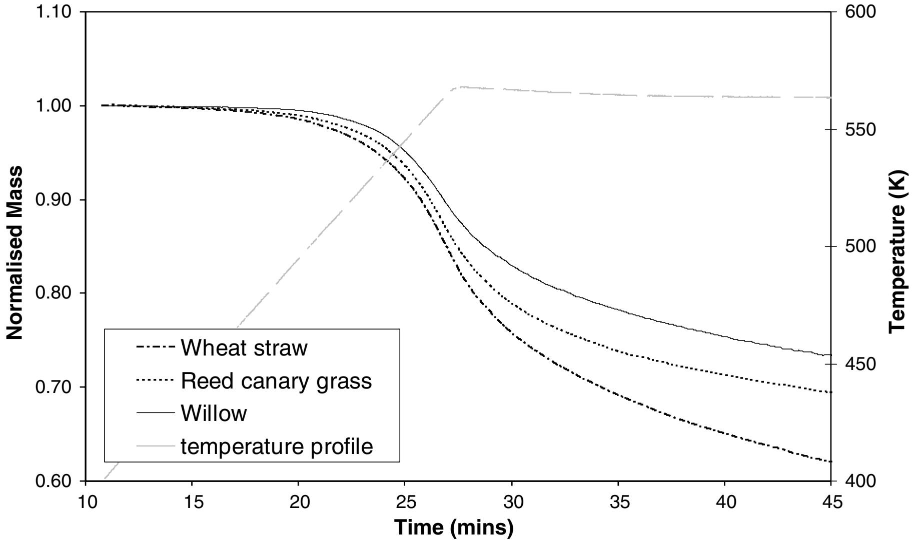

Fig. 2. Mass loss of wheat straw, reed canary grass and willow during torrefaction at 563 K.

Table 1
Mass% of hemicellulose, cellulose and lignin in raw biomass fuels (dry ash free basis)

	Lignin (%)	Cellulose (%)	Hemicellulose (%)	Total (DMD) (%)
Reed canary gass	7.6	42.6	29.7	80.0
Wheat straw	7.7	41.3	30.8	79.8
Willow	20.0	49.3	14.1	83.4

polysaccharide will devolatise [21]. However, a number of studies have concluded that accompanying this observed mass loss are depolymerisation reactions that reduce the length of the polysaccharide polymers from 1000 to 200 monomer units [22]. Further work will look more closely at the behaviour of the individual cell wall components during torrefaction.

The thermal decomposition of biomass within torrefaction temperatures yields a number of different products. Water is the major product and is released in two different mechanisms, firstly during drying when moisture evaporates and secondly during dehydration reactions between organic molecules. However, there are a number of other organic and inorganic products present in the volatile component liberated during the decomposition of biomass. Fig. 3 was obtained from the FTIR spectra measured during the torrefaction of reed canary grass at 563 K and shows the evolution profiles of the main gaseous and volatile constituents detected. The peak of the absorbance curves indicates the point of maximum thermal decomposition of the biomass sample and corresponds with the differential mass loss curve.

The gaseous products detected were carbon dioxide, carbon monoxide and methane. The remaining products comprised of condensable organics. These included formaldehyde, acetaldehyde, acetic acid, formic acid, acetone and methanol. Traces of phenol, furfural and ammonia were also detected for the highest temperature treatments (see Fig. 3).

3.1.2. CHN and calorific values

Ultimate analysis of the fuels revealed the alterations that occur in the chemical composition of biomass when it is exposed to torrefaction conditions: the carbon content was increased, whilst decreases were observed in the hydrogen and oxygen content. The exception is nitrogen content which remained almost constant. Calculation of the HHV illustrates the impact that these changes have on the energy content (Table 2). During the reactions the liberated compounds contain higher proportions of oxygen and hydrogen than carbon, thus reducing the relative concentration of these elements in the solid residue.

Fig. 4 illustrates the effect that increasing temperatures have on the carbon, hydrogen and oxygen content of the three fuels. Despite larger mass losses the increase in the carbon content of reed canary grass was very similar to that of willow. However, torrefaction of willow caused a greater reduction in oxygen content than that of reed canary grass but in contrast this trend was reversed for hydrogen. The overall result is that treatment at 563 K caused an increase in the energy content of approximately 12% in both fuels. Wheat straw undergoes the most compositional transformations and for all four temperatures investigated the loss of hydrogen and oxygen and the increase in carbon was greater than willow or reed canary grass. The energy content of wheat straw torrefied at 563 K rose by 17%.

A plot of the molecular ratios of carbon, hydrogen and oxygen on the Van Krevelen diagram, Fig. 5, shows that the change in elementary composition of torrefied biomass moves it towards lignite on the Van Krevelen plot. From this diagram it can be observed that of the three types of samples investigated, torrefaction had the biggest effect on wheat straw regarding alterations of its fuel properties.

3.1.3. Energy balance

The dry ash free mass and energy yields of the solid residues were calculated, based on equations suggested by Bergman et al. [4]:

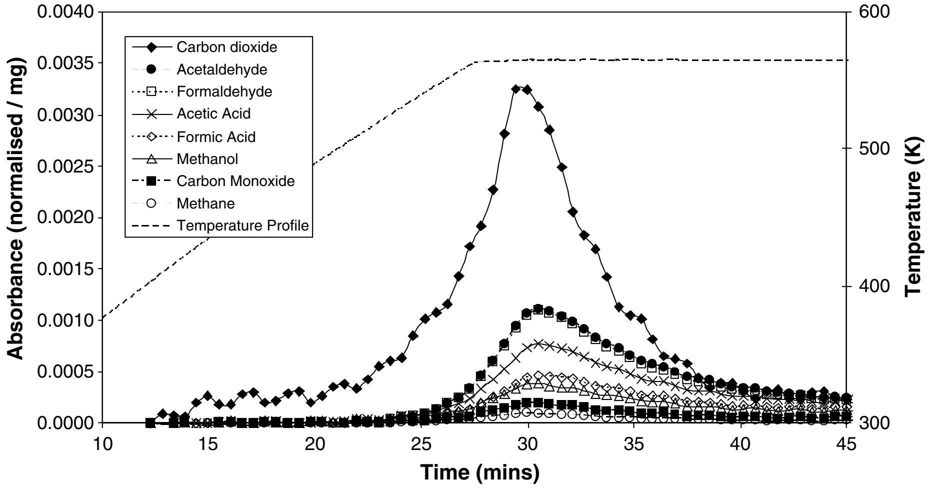

Fig. 3. Evolution of volatile products during torrefaction of reed canary grass at 563 K.

Table 2
Ultimate analysis, HHV (dry ash free basis), and moisture content of untreated and torrefied biomass fuels

	Raw	Torrefaction temperature (K)			
		503	523	543	563
RCG					
C (%)	48.6	49.3	50.3	52.2	54.3
H (%)	6.8	6.5	6.3	6.0	6.1
N (%)	0.3	0.1	0.0	0.1	0.1
O (%)	37.3		37.0	37.3	36.3
Moisture (%)	4.7	2.5	1.9	1.3	1.2
CV (kJ/kg)	19,500	–	20,000	20,800	21,800
Wheat straw					
C (%)	47.3	48.7	49.6	51.9	56.4
H (%)	6.8	6.3	6.1	5.9	5.6
N (%)	0.8	0.7	0.9	0.8	1.0
O (%)	37.7		35.6	33.2	27.6
Moisture (%)	4.1	1.5	0.9	0.3	0.8
CV (kJ/kg)	18,900	19,400	19,800	20,700	22,600
Willow					
C (%)	49.9	50.7	51.7	53.4	54.7
H (%)	6.5	6.2	6.1	6.1	6.0
N (%)	0.2	0.2	0.2	0.2	0.1
O (%)	39.9	39.5	38.7	37.2	36.4
Moisture (%)	2.8	0.5	0.1	0.1	0.0
CV (kJ/kg)	20,000	20,200	20,600	21,400	21,900

$$Y_{\text{mass}}(\%) = \left(\frac{m_{\text{product}}}{m_{\text{feed}}}\right)_{\text{daf}} \times 100 \tag{3}$$

$$Y_{\text{energy}}(\%) = Y_{\text{mass}}\left(\frac{HHV_{\text{product}}}{HHV_{\text{feed}}}\right)_{\text{daf}} \tag{4}$$

Higher heating values were calculated from Eqs. (1) and (2) using elementary analysis results of all the fuels given in Table 2. The results of the energy and mass yield calculations are shown in Fig. 6. For all products of torrefaction the energy yield was greater than the mass yield – an effect which became more marked for higher temperature treatments. The greatest difference between energy yield and mass yield occurred in wheat straw torrefied at 563 K (10.7%). Reed canary grass and willow showed a similar pattern for mass yield and energy yield differences. For 503, 523, 543 and 563 K treatments the differences were 0.9%, 2.6%, 5.1% and 7.5% respectively for reed canary grass. For willow these figures were 1.4%, 3.1%, 5.9%, and 7.2% respectively.

3.2. Fuel properties

3.2.1. Pyrolysis of torrefied biomass

The pyrolysis profiles of reed canary grass and torrefied reed canary grass are shown in Fig. 7. Mass loss curves (not

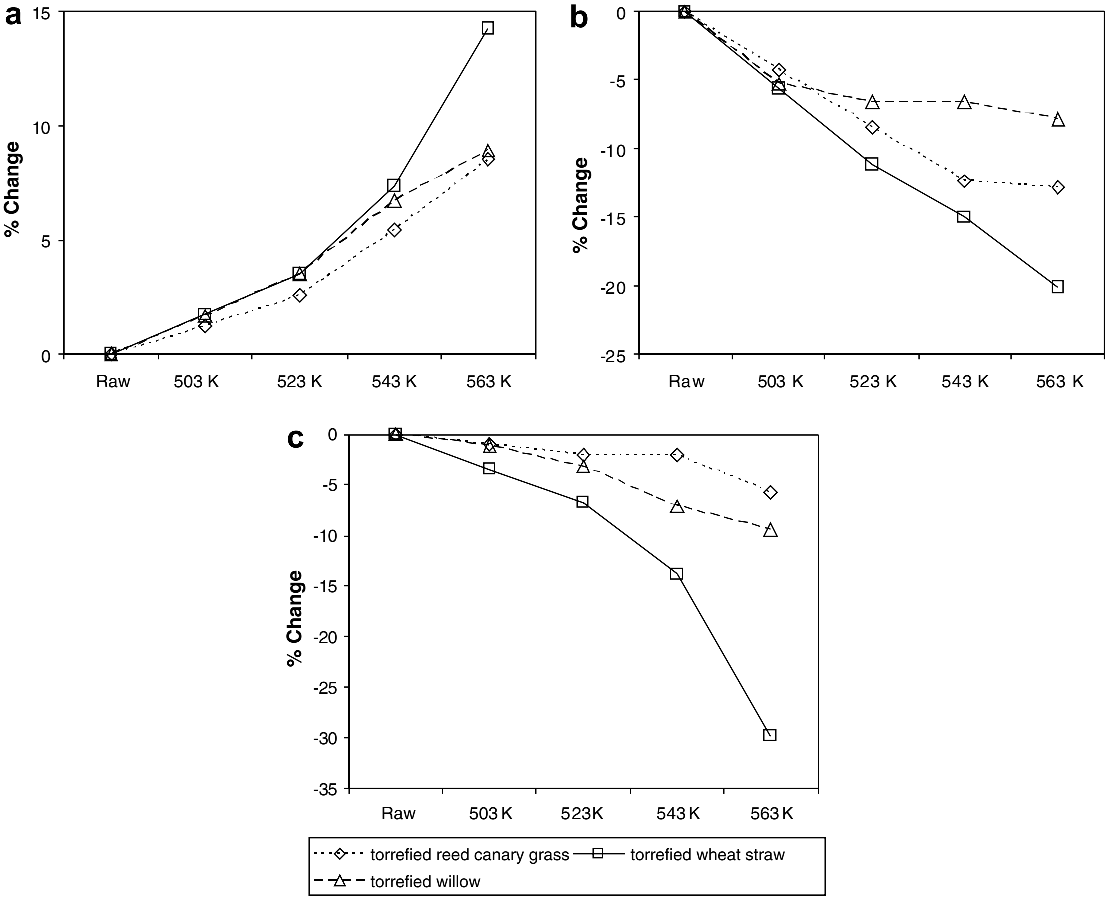

Fig. 4. Changes in elemental composition as a result of torrefaction treatment at four different final temperatures: (a) carbon; (b) hydrogen; (c) oxygen.

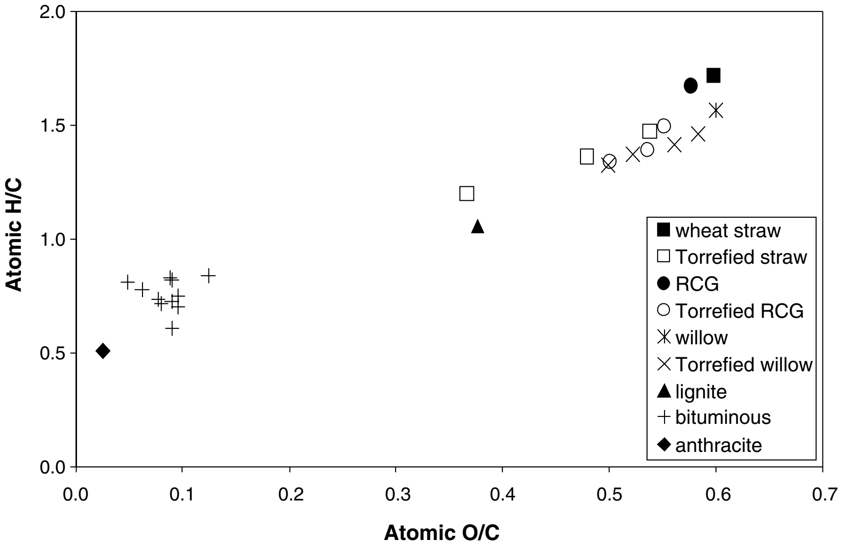

Fig. 5. Van Krevelen diagram for coals, biomass and torrefied biomass.

shown) and proximate data in Table 3 reveal the lower volatile content of torrefied fuels. In addition, the onset of volatile release occurs at higher temperatures for samples which have undergone torrefaction at higher temperatures. Devolatilisation of raw wheat straw (not shown) commenced at temperatures approximately 100 K lower than straw torrefied at 563 K. For reed canary grass and willow (not shown) the difference was approximately 50 K.

For untreated reed canary grass and willow there are two stages of devolatilisation during pyrolysis as seen by an initial ‘shoulder’ (willow) and smaller adjacent peak (reed canary grass) to the main volatile release peak. This is associated with the release of light volatile products occurring from thermal decomposition at lower temperatures, and attributable to the decomposition of hemicellulose. Torrefaction above 543 K removed this peak. There is negligible change in the position of the peaks on the temperature axis of the DTG curves.

3.2.2. Burning profiles

Fig. 8 shows the burning profiles of raw and torrefied reed canary grass. A narrowed peak for volatile combustion was observed for the torrefied samples, most noticeable for the products of the 563 K treatment. This indicated a shorter period of time and narrower range of temperatures for this event to occur, suggesting that a faster rate of volatile combustion occurred. The shoulder observed in the pyrolysis DTG curve of raw reed canary grass is also observed during heating in air. Similarly, this is not present during combustion of reed canary grass torrefied at temperatures of 543 K or 563 K. The maximum points of the mass loss curves for the torrefied samples were slightly shifted to lower temperatures. This shift was more pronounced for samples torrefied at higher temperatures.

The results from TGA experiments conducted in nitrogen and air were used to determine proximate analysis of the fuels and these are presented in Table 3. The volatile, fixed carbon and ash contents are given for the dry sample. The trend is a reduction in moisture content and volatile matter and an increase in fixed carbon and ash content. As seen in other analysis of the fuels, wheat straw underwent the most significant changes. For example, the reduction in volatile matter for the product of torrefaction at 563 K was 21% for wheat straw (from 72.8% to 51.8%), whereas for willow this figure was only 10.4% (87.6% to 77.2%).

3.2.3. Differential thermal analysis (DTA)

The area enclosed by the DTA curve is given by [23]:

$$\frac{m \cdot \Delta H}{gk} = \int_{t_1}^{t_2} \Delta T \cdot \mathrm{d}t \tag{5}$$

where m is the mass of sample (mg); ΔH is the heat of reaction (kJ mol^{-1}); g is the geometric shape constant for the apparatus ($4\pi h$ or $8\pi a$; h is the height of sample, a is the radius of sample holder) (m); k is the thermal conductivity (W m^{-1} K^{-1}); ΔT is the differential temperature (K); t_1 and t_2 are the integral limits of differential curve (K).

The DTA data was normalised for mass. It was assumed that the thermal conductivity of the torrefied samples remains the same as the raw biomass samples, and a direct comparison of the heats of reaction for the volatile and char combustion reactions (and hence the total combustion reactions) of raw and torrefied fuels was made using Eq. (6) below. The subscripts a and b correspond to *fuel a* and *fuel b* respectively.

$$\frac{gk_{\mathrm{a}}\left[\int_{t_1}^{t_2} \frac{\Delta T_{a1}}{m_{\mathrm{a}}} \cdot \mathrm{d}t\right]}{gk_{\mathrm{b}}\left[\int_{t_1}^{t_2} \frac{\Delta T_{\mathrm{b}}}{m_{\mathrm{b}}} \cdot \mathrm{d}t\right]} = \frac{\Delta H_{\mathrm{a}}}{\Delta H_{\mathrm{b}}} \tag{6}$$

The differential temperature curves were also analysed to determine the start point and end point of the differential

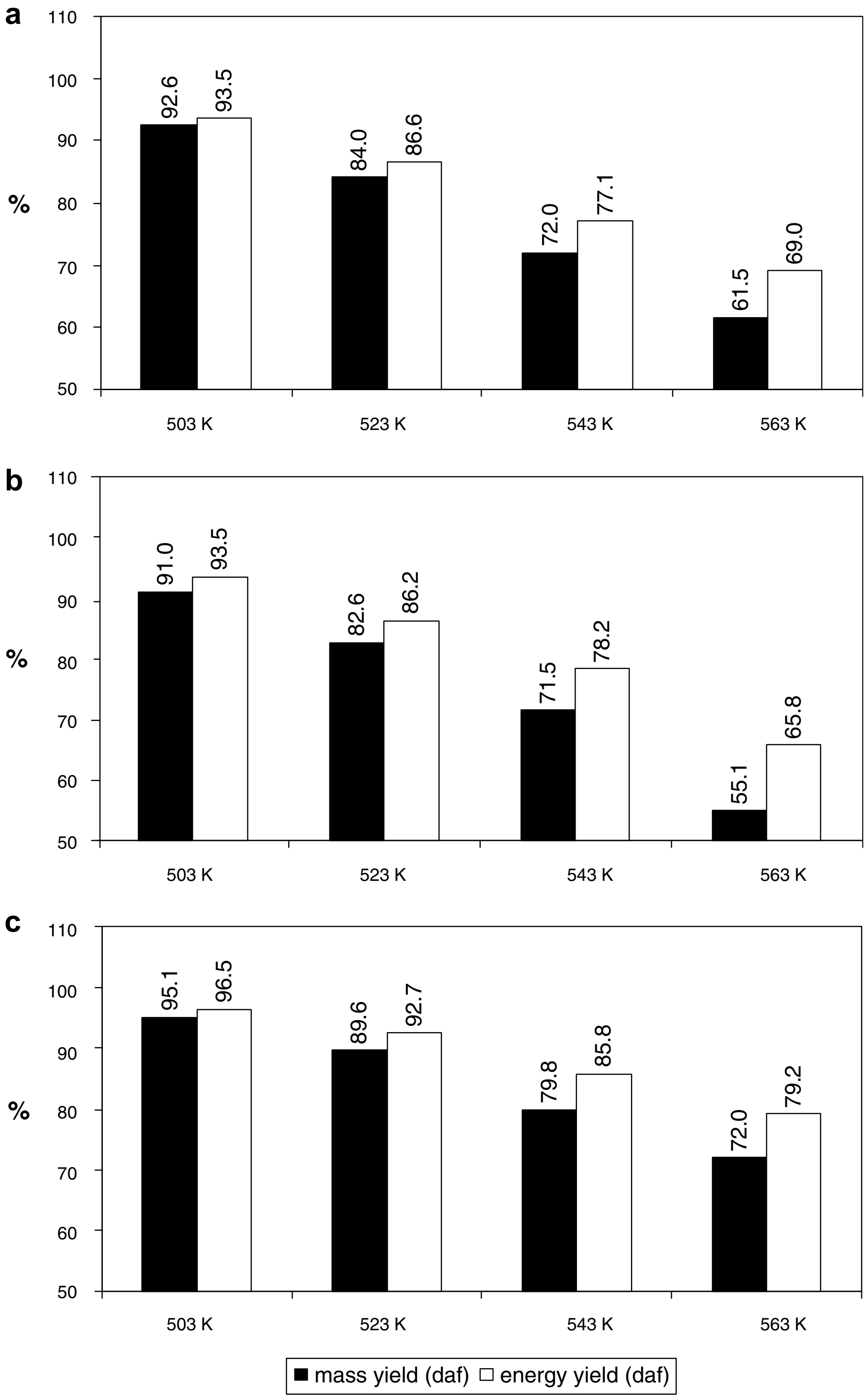

Fig. 6. Mass and energy yields (dry ash free) for (a) reed canary grass; (b) wheat straw; (c) willow at treated at temperatures of 503, 523, 543 and 563 K (reaction time of 30 mins).

curve, as well as the peak locations. Fig. 9 shows the points of interest on a typical DTA curve from biomass combustion along with a comparison of the DTA curves produced from raw and torrefied reed canary grass. Table 4 shows the complete set of data obtained from the DTA curves of reed canary grass and wheat straw combustion.

It was observed that combustion of torrefied biomass produced higher heats of reactions during combustion and these increase for fuels produced at higher torrefaction temperatures. The lower values for raw biomass were partly attributable to the higher moisture content of these fuels, as the curves were normalised for mass on an as received basis. However, despite lower volatile content of

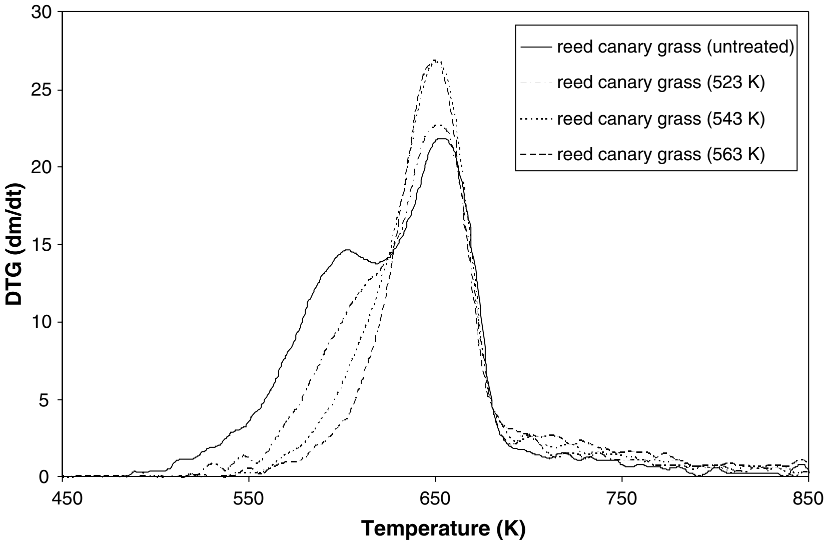

Fig. 7. Devolatisation profiles of untreated reed canary grass and reed canary grass torrefied at final temperatures of 523, 543 and 563 K.

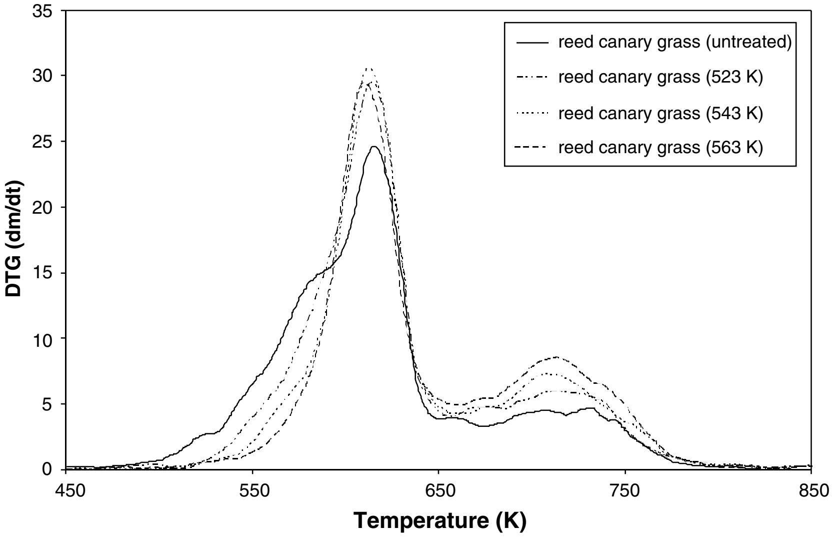

Fig. 8. Burning profiles of untreated reed canary grass and reed canary grass torrefied at final temperatures of 523, 543 and 563 K.

torrefied wood, the combustion of the remaining volatiles produced a greater heat of reaction and a large maximum differential temperature. This maximum differential temperature peak also shifted to lower temperatures for products of higher temperature treatment. Additionally, the onset of volatile combustion was shifted to lower temperatures, again with this effect increasing for fuels produced from higher torrefaction treatments.

The maximum differential temperature occurring during char combustion was also observed to increase, and this can be accounted for by higher fixed carbon content within the fuels (see Table 3).

Comparison of the DTA and DTG on the same plots for raw and torrefied reed canary grass indicates that the onset of a significant differential temperature occurred earlier and for a correspondingly smaller actual mass loss for torrefied biomass. Indeed, the start point for mass loss during combustion occurred at increasingly higher temperatures for torrefied biomass treated at higher temperatures. Combining this information with the previous results suggests that the initial stage of combustion of torrefied biomass occurred without a large mass loss. In contrast during the initial stage of combustion of raw reed canary grass significant mass loss occurred without producing significant differential temperatures.

These observations could be explained by two possibilities. One explanation is that the low weight volatiles produced from biomass during the early stages of thermal decomposition (in a reactive atmosphere) have low energy contents and low heats of combustion. The resultant energy may be comparable to the energy required for their liberation with the net energy balance being negligible. Alternatively, a second explanation is that the lowest weight molecules that evolve from untreated biomass are

Table 3
Proximate analysis (TGA) of raw and torrefied fuels

	Raw	Torrefaction temperature (K)			
		503	523	543	563
RCG					
Moisture content (%)	4.7	–	1.9	1.3	1.2
Volatile matter[a] (%)	82.5	–	80.3	76.6	70.5
Ash content[a] (%)	5.5	–	6.4	7.3	8.3
Fixed carbon[a] (%)	12.1	–	13.3	16.1	21.3
Wheat straw					
Moisture content (%)	4.1	–	0.9	0.3	0.8
Volatile matter[a] (%)	76.4	–	77.0	65.2	51.8
Ash content[a] (%)	6.3	–	7.4	8.4	10.2
Fixed carbon[a] (%)	17.3	–	15.6	26.5	38.0
Willow					
Moisture content (%)	2.8	0.5	0.1	0.2	0.0
Volatile matter[a] (%)	87.6	82.1	79.8	79.3	77.2
Ash content[a] (%)	1.7	1.8	1.9	2.1	2.3
Fixed carbon[a] (%)	10.7	16.1	18.4	18.6	20.5

[a] Volatile matter, ash content and fixed carbon expressed on a dry basis.

mostly non-combustible (i.e. H_2O, CO_2) and merely devolatilise from the fuel without combusting at all, and it is not until the release of volatile organics at higher temperatures that ignition occurs. Some low weight molecules have been removed from torrefied biomass, and the volatile products released in the early stages of thermal decomposition are both combustible and of a higher calorific value thus producing instantaneous differential temperatures that are seen on the DTA curves from the combustion of torrefied reed canary grass, willow and wheat straw.

Furthermore, the DTA results suggest that ignition of the volatile matter occurred at lower temperatures and complete combustion of volatile matter in torrefied wood occurred over a shorter time period in comparison with the raw fuel. This latter observation can be explained by a lower volatile content with altered composition. However, it may also be assisted by an increased surface area of the partial char residue allowing for increased solid–gas mass transfer. Measurements using BET surface area

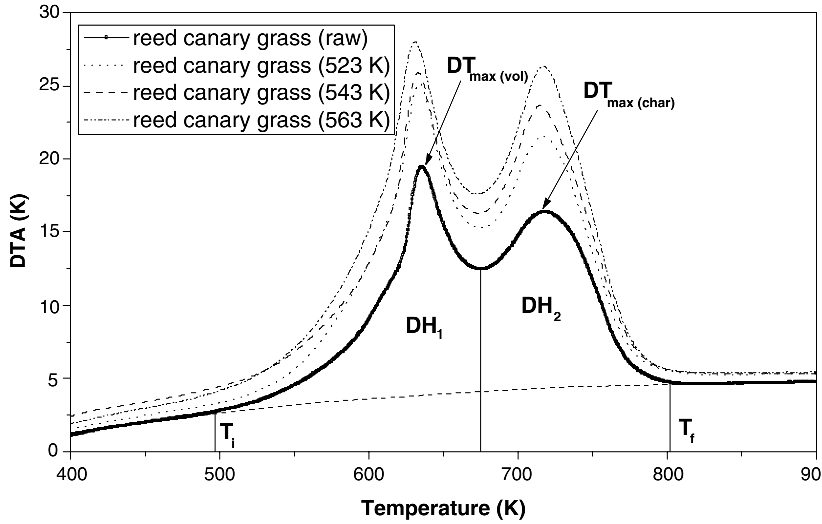

Fig. 9. Differential thermal analysis of untreated reed canary grass and reed canary grass torrefied at final temperatures of 523, 543 and 563 K during combustion in air at a heating rate of 20 K min^{-1}. T_i – procedural initial deviation temperature detected by the instrument; ΔT_{max} – procedural peak maximum temperature; T_f – procedural final deviation temperature of the curve peak; ΔH – the heat of combustion per unit mass (area beneath curve).

Table 4
Differential thermal analysis of raw and torrefied biomass

Fuel	T_i (K)	Volatile combustion				Char combustion				Overall		T_f (K)
		ΔT_{max} (K)	T at ΔT_{max} (K)	ΔH_1		ΔT_{max}(K)	T at ΔT_{max} (K)	ΔH_2		ΔH_{total}		
				Actual	Relative			Actual	Relative	Actual	Relative	
RCG (raw)	485	15.7	635	41.8	1.00	12.1	717	42.2	1.00	84.0	1.00	816
RCG (523 K)	482	21.1	634	58.5	1.40	16.9	716	56.7	1.34	115.2	1.37	821
RCG (543 K)	473	21.1	633	58.2	1.39	18.6	715	60.9	1.44	119.1	1.42	823
RCG (563 K)	464	23.4	631	68.8	1.65	21.4	717	70.0	1.66	138.7	1.65	815
Straw (raw)	470	23.2	611	72.8	1.00	16.3	691	61.6	1.00	134.4	1.00	808
Straw (523 K)	455	27.6	612	83.5	1.11	20.3	690	78.7	1.26	162.2	1.17	805
Straw (543 K)	455	32.3	612	97.6	1.36	21.0	692	79.4	1.29	177.0	1.33	825
Straw (563 K)	431	38.1	606	108.8	1.51	24.9	688	92.8	1.49	201.6	1.50	803

of willow revealed that the total surface area of willow particles of 212–355 μm increased from 1.50 m^2/g for the raw willow to 2.30 m^2/g for willow treated at 563 K.

3.2.4. Combustion studies in a methane air flame

The torrefied willow fuels were also studied for their combustion behaviour under conditions of high heating rate and high temperature. The individual particles were suspended in a methane air flame and their combustion events were recorded using a high speed camera at 1000 fps. Fig. 10a and b illustrate the burning times for the volatile and char stages of combustion of raw and torrefied willow particles. It was seen that the volatile combustion times were slightly reduced as a result of torrefaction whereas the times for char burnout increased for higher temperatures of torrefaction. The combined burning times for both stages (Table 5) show that overall the times for combustion are increased. This is mainly because they are dominated by the char combustion stage; a result of the decreased volatile content and the increased char content in torrefied particles (see Table 3). However it should be noted that these two events overlapped, and whilst the area of the particle furthest from the heat source was still undergoing pyrolysis, the lower part of the particle had already formed a char.

The average ignition times (assumed to be independent of particle mass) of the different particles investigated are presented in Table 6. Generally torrefied particles had

Table 5
Complete combustion times for raw and torrefied willow particles

Particle mass (mg)	Combustion times of fuel particles (s)		
	Willow (Raw)	Willow (523 K)	Willow (563 K)
0.5	4.8	7.4	12.3
1.0	6.8	11.4	16.9
1.5	8.0	13.7	19.6

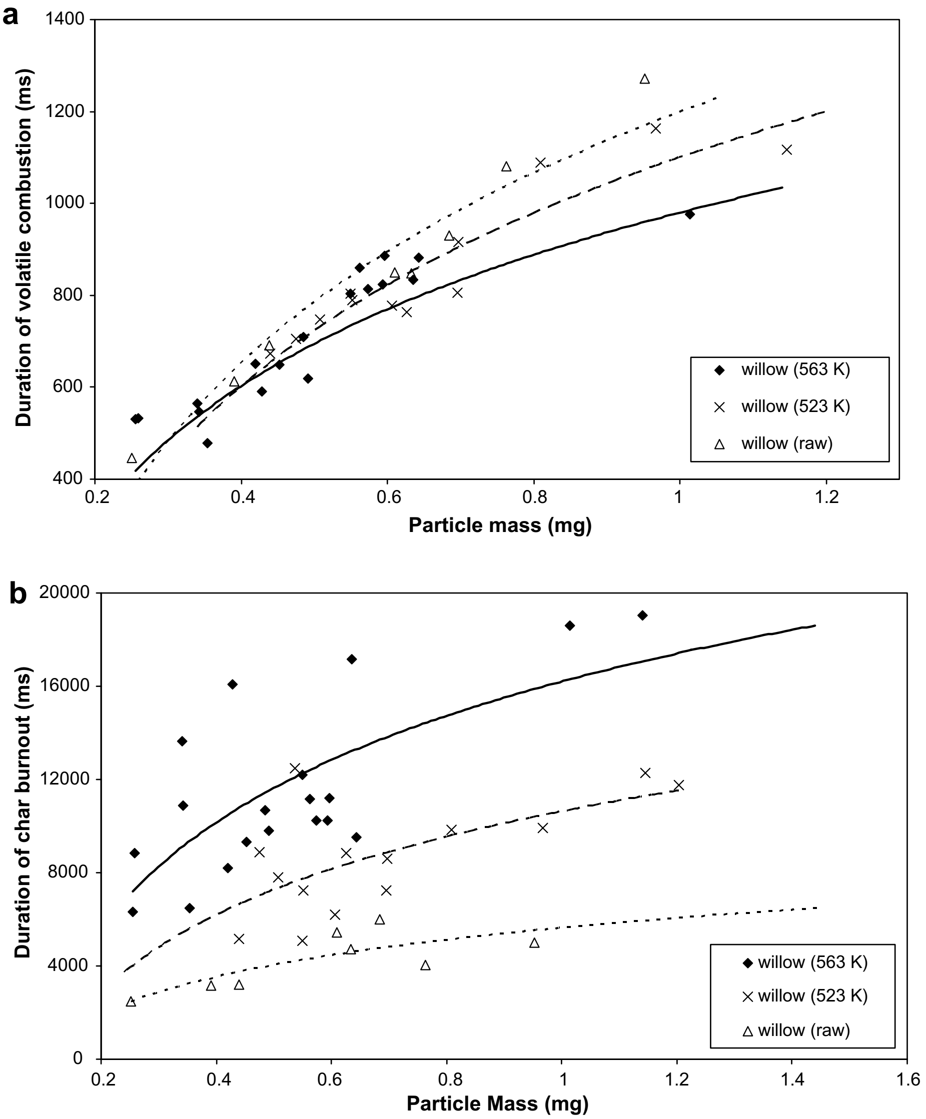

Fig. 10. Combustion times of (a) volatile and (b) char of individual raw willow particles and willow particles torrefied at temperatures of 523 and 563 K.

Table 6
Volatile and char ignition times of raw and torrefied willow particles

	Volatile ignition data (ms)		Char ignition data (ms)	
	Average	Standard deviation	Average	Standard deviation
Willow (raw)	153	28	793	163
Willow (523 K)	109	9	629	120
Willow (563 K)	104	19	347	107

reduced ignition times for volatile and char combustion, although this pattern is most noticeable for char combustion. For particles treated at 563 K, the ignition times of the char were halved. Earlier char combustion was inhibited whilst devolatilisation occurred in other parts of the particle and it was not until completion of the volatile combustion stage that the char burnout proceeded at a fast rate and involved the whole particle (observed by the entire particle glowing orange).

4. Conclusions

Herbaceous biomass undergoes greater alterations in its properties during torrefaction than woody biomass, in terms of mass loss and atomic composition. The overall mass loss in both herbaceous species investigated was similar but wheat straw underwent greater changes in terms of it elemental composition and increases in energy content: carbon content rose by a maximum of 14% to 51 wt%, oxygen content was reduced by 30% to 25% and the energy content rose by 20% to 22.6 MJ kg^{-1}. However, the overall energy yield was slightly lower for wheat straw. In contrast the mass and energy yields of willow were noticeably higher than the two herbaceous species. For example, after treatment at 543 K the mass yield of willow was 80%, whereas the figures for wheat straw and reed canary grass were 72% and 71%, respectively. The energy yields for these conditions were 77%, 78% and 86% for wheat straw, reed canary grass and willow respectively. However, willow torrefied at 563 K only experienced an increase in its overall energy content of 9.5% These observed differences appear to be mostly attributed to differences in the lignocellulose composition of the fuels, specifically the higher hemicellulose content of graminaceous crops.

Observations of combustion behaviour revealed a number of differences between torrefied biomass and raw fuels. For all fuels, volatile combustion was modified and occurred over a shorter temperature range and the herbaceous crops produced heats of combustion that were between 10–65% higher, depending on the treatment temperature and crop. The higher fixed carbon content also meant that torrefied biomass produced greater heats of combustion during char burnout. All these observed behavioural changes were more pronounced for the products of higher torrefaction temperatures. From DTA and the analysis of high speed videos of the combustion of untreated and torrefied willow particles it was observed that the ignition times of both combustible volatiles and char were reduced as a result of torrefaction. These changes in properties are expected to be beneficial during combustion applications.

It is suggested that future work investigates the change in nature of the composition of volatile component of torrefied fuels and should seek to identify any potential benefits for other thermochemical conversion processes.

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